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(71) Applicant: **JSC " Avisma Titanium-Magnesium
Works"**

Permskaya obl., 618421 (RU)

(72) Inventors:

- **TETYUKHIN, Vladislav Valentinovich**
Sverdlovskaya obl., 624600 (RU)

• **AGALAKOV, Vadim Vladimirovich**

Permskaya obl., 618400 (RU)

• **KORNAUKHOVA, Lyudmila Fedorovna**

Sverdlovskaya obl., 624600 (RU)

• **PUSCHKAREV, Sergey Yurevich**

Permskaya obl., 618400 (RU)

(74) Representative: **Rupprecht, Kay, Dipl.-Ing.**

Meissner, Bolte & Partner

Postfach 86 06 24

81633 München (DE)

(54) MAGNESIUM-BASED ALLOY AND METHOD FOR THE PRODUCTION THEREOF

(57) The invention relates to magnesium-based alloys and, in particular, to magnesium alloy composition and methods of producing the same that are now widely used in the automotive industry.

Said invention makes it possible to reduce the production costs of the alloy and to improve the performance characteristics thereof in order to extend the use of said alloy for the automobile industry.

These objects are accomplished due to the fact that the claimed magnesium-based alloy comprises aluminium, zinc, manganese and silicon, **wherein** the constituents specified are in the following components, wt.%:

Aluminium - 2.5-3.4

Zinc - 0.11-0.25

Manganese - 0.24-0.34

Silicium - 0.8-1.1

Magnesium - rest being

To manufacture the alloy there is a method for producing which consists in loading of alloying components, pouring of molten magnesium, introducing a titanium-containing fusion cake together with a flux agent and continuous agitation, and the alloy is soaked and casted, wherein in loading alloying components of aluminium, zinc, manganese, and silicon in the form of a ready-made solid master alloy of aluminium-zinc-manganese-silicium master alloy, after poured in the magnesium is heated, subjected to ageing and then stirred. Further, the proportion of the master alloy to magnesium is 1: (18-20).

Further, magnesium is heated up to 720-740°C.

Further, the ageing process lasts for 1-1.5 hrs.

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Description

Field of the Invention

5 [0001] This invention relates generally to magnesium-based alloys and more specifically to magnesium alloy composition and methods of producing them that are widely used in the automotive industry.

Background of the invention

10 [0002] There are various alloys developed for special applications including, for example, die casting of automotive components. Among these alloys magnesium-aluminium alloys can be designated as cost-effective and widely used for manufacture of automotive parts, e.g. AM50A alloy (where AM means aluminium and manganese are in the composition of the alloy) containing approx. 5 to 6 wt.% aluminium and manganese traces, and magnesium-aluminium-zinc alloys, e.g. AZ91D (where AZ means aluminium and zinc are in the composition of the alloy) containing approx.
15 9 wt.% aluminium and 1 wt.% zinc.

[0003] The disadvantage of these alloys is their low strength and poor creep resistance at elevated operating temperatures. As a result, the above mentioned magnesium alloys are less suitable for motor engines where some components such as transmission cases are exposed to temperatures up to 150°C. Poor creep resistance of these components can lead to a decrease in fastener clamp load in bolted joints and, hence, to oil leakage.

20 [0004] Known in the present state of art is a magnesium-based alloy (Inventors' certificate No. 442225 issued in *Invention Bulletin* 33, 1974) containing aluminium, zinc, manganese, silicon as alloying components in the following contents:

25 Aluminium - 6-15 wt.%
Zinc - 0.3-3.0 wt.%
Manganese - 0.1-0.5 wt.%
Silicon - 0.6-2.5 wt.%
Magnesium - rest being

30 [0005] The disadvantages of this alloy are its low ductility, high hot shortness, and insufficient strength of the alloy which keeps this alloy from automotive applications.

[0006] Known presently is another magnesium die cast alloy ("Magnesium alloys" in *Collected works of Baikov Institute for Metallurgy* edited by Nauka Publishing House, 1978, p.140-144) which comprises aluminium, zinc, manganese, silicon as alloying components in the following contents:

35 Aluminium - 3.5-5.0 wt.%
Zinc - under 0.12 wt.%
Manganese - 0.20-0.50 wt.%
Silicon - 0.5-1.5 wt.%
40 Copper - under 0.06
Nickel - 0.03 wt.%

[0007] The drawback of this alloy is that the quantitative composition of the alloy selected provides poor mechanical properties, in particular, the alloy having a small solidification range is characterised with advanced susceptibility to cracking in case of hindered contraction and bad castability.

45 [0008] A well-known German standard EN 1753-1997 is taken as the closest prior art by its qualitative and quantitative composition and discloses the methods of manufacture of EN MB MgAl₂Si and EN MB MgAl₄Si alloys.

The qualitative analysis of the alloys is the following, in wt.%:

50 EN MB MgAl₂Si:

Al - 1.9-2.5
Mn - min 0.2
Zn - 0.15-0.25
55 Si - 0.7-1.2

EN MB MgAl₄Si (AS41):

Al - 3.7-4.8
 Mn - 0.35-0.6
 Zn - max 0.10
 Si - 0.6-1.4

[0009] The alloys of the above quantitative and qualitative composition demonstrate better mechanical properties. However, at 150-250°C these alloys have high creep that keeps these alloys from machine-building application. Presently known is the method (PCT Patent No.94/09168) for making a magnesium-based alloy that provides for alloying components in a molten state being introduced into molten magnesium. Primary magnesium and alloying components are therefor heated and melted in separate crucibles.

[0010] What is disadvantageous of this method is the need to pre-melt manganese and other alloying elements (at the melting temperature of 1250°C) that complicates alloy production and process instrumentation.

[0011] There are some other methods known (B.I.Bondarev "Melting and Casting of Wrought Magnesium Alloys" edited by Metallurgy Publishing House, Moscow, Russia 1973, pp 119-122) to introduce alloying components using a master alloy, e.g. a magnesium-manganese master alloy (at the alloying temperature of 740-760°C).

This method is disadvantageous because the alloying temperature should be kept high enough which leads to extremely high electric power consumption for metal heating and significant melting loss.

[0012] Also known is another method of producing a magnesium-aluminium-zinc-manganese alloy (I.P. Vyatkin, V. A. Kechin, S.V. Mushkov in "Primary magnesium refining and melting" edited by Metallurgy Publishing House, Moscow, Russia 1974, pp.54-56, pp.82-93) which is taken as an analogue-prototype. This method stipulates various ways how to feed molten magnesium, alloying components such as aluminium, zinc, manganese. One of these approaches includes simultaneous charging of solid aluminium and zinc into a crucible, then heating above 100°C, pouring in molten primary magnesium and again heating up to 700-710°C and introducing titanium-containing fusion cake together and manganese metal under continuous agitation.

[0013] The main shortcoming of the method is in considerable loss of alloying components resulting in lower recovery of alloying components in magnesium and preventing from producing alloys with specified mechanical properties. Furthermore, this increases the cost of the alloy.

Summary of the Invention

[0014] Accordingly, it is an object of the present invention to improve mechanical properties of the alloy and, in particular, to decrease its creep and loss of alloying constituents in manufacturing the alloy.

[0015] Said invention makes it possible to reduce the production costs of the alloy and to improve the performance characteristics thereof in order to extend the use of said alloy for the automobile industry.

[0016] These objects are accomplished due to the fact that the claimed magnesium-based alloy comprises aluminium, zinc, manganese and silicon, wherein the constituents specified are in the following components, wt.%:

Aluminium - 2.5-3.4
 Zinc - 0.11-0.25
 Manganese - 0.24-0.34
 Silicon - 0.8-1.1
 Magnesium - rest being

[0017] To manufacture the alloy there is a method for producing which consists in loading of alloying components, pouring of molten magnesium, introducing a titanium-containing fusion cake together with a flux agent and continuous agitation, and the alloy is soaked and casted, wherein in loading alloying components of aluminium, zinc, manganese, and silicon in the form of a ready-made solid master alloy of aluminium-zinc-manganese-silicon master alloy, after poured in the magnesium is heated, subjected to ageing and then stirred.

Further, the proportion of the master alloy to magnesium is 1: (18-20).

Further, magnesium is heated up to 720-740°C.

Further, the ageing process lasts for 1-1.5 hrs.

[0018] Said quantitative composition of the magnesium-based alloy enables better mechanical properties of the alloy.

[0019] Aluminium added into magnesium contributes to its tensile strength at ambient temperature and alloy castability. However, it is well-known that aluminium is detrimental to creep resistance and strength of magnesium alloys at elevated temperatures. This results from the case that aluminium, when in higher contents, tends to combine with magnesium to form great amounts of intermetallic $Mg_{17}Al_{12}$ having a low melting temperature (437°C) which impairs high-temperature properties of aluminium-based alloys. Aluminium content of 2.5-3.4 wt. % that was chosen for the proposed magnesium-based alloy provide better properties of magnesium-based alloys, such as creep resistance.

[0020] The properties of the alloy, especially its castability, are further influenced by zinc content; however, added in large amounts, zinc can lead to cracking. Therefore, proposed zinc content is within 0.11-0.25wt.% to be optimum for the magnesium-based alloy.

[0021] In order to enhance service performance and functionality and expand the scope of application at higher temperatures (up to 150-200°C) silicon is added into the alloy as an active alloying additive to form a metallurgic stable phase Mg_2Si precipitated slightly at grain boundaries and, hence, to increase creep resistance of the alloy at high temperatures. Silicon content of 0.8-1.1 wt. % claimed in accordance with the present invention enables decreasing creep level of the magnesium-based alloy.

[0022] The alloy is loaded with manganese in the content 0.24-0.34 wt. % in order to ensure corrosion resistance.

[0023] The alloying components are introduced in the form of the pre-prepared aluminium-zinc-manganese-silicon master alloy, which is added in the certain proportion to magnesium, i.e. 1 : (18-20), and this, therefore, enhances recovery of the additives in magnesium, thus lowering losses of expensive chemicals.

It is another difficulty in making alloys with silicon content that silicium and manganese as alloying components come to a reaction forming heavy intermetallic phases Mn_3Si and $MnSi_2$, which deposit at the bottom of crucibles at the end of production process, and this hinders high level of recovery of these components. Thus, a better recovery of the alloying additives can be produced using the pre-prepared aluminium-based master alloy.

With process temperature maintained at 720-740°C the level of recovery of alloying elements in magnesium can be 98.8-100% in case of aluminium, 68.2-71.1% in case of manganese, 89.3-97.4 in case of silicon, 85.9-94.4% in case of zinc.

Detailed description of preferred embodiments

Preparation of Al-Mn-Si-Zn master alloy

[0024] Composition: aluminium - matrix, manganese - 6.0-9.0 wt.%, silicium - 24.0-28.0 wt. %, zinc - 2.0-3.0 wt. %, inclusions, in wt. %: iron - 0.4, nickel - 0.005, copper - 0.1, titanium - 0.1. The master alloy is produced in ingots.

The master alloy is manufactured in an 'AIX'-type induction furnace. A97 grade aluminium (acc. to GOST 11069) is charged in the furnace, heated up to 910-950°C; the master alloy is melted under cryolite flux in the amount of 1-1.5% of the pre-weighted quantity required for the process. Kp1 (Kr1) grade crystalline silicon is fed in portions in the form of crushed pieces, it is a possible means that the pieces of silicium be wrapped in aluminium foil or wetted with zinc chloride solution to prevent them from oxidation. Silicium is dissolved in small portions being thoroughly stirred. The composition obtained is thereafter added with manganese metal of M_H95 grade (Mn95 acc. to GOST 6008) in the form of 100 mm pieces, stirred again and heated up to the temperature within 800-850°C; finally added with II1-grade zinc (Z1 acc. to GOST 3640). 16 kg ingots are cast in moulds.

Example 1

[0025] Solid master alloy of Al-Mn-Si-Zn in the form of ingots in the proportion of master alloy to magnesium 1 : (18-20) are charged into a preheated crucible of furnace SMT-2, in the same crucible raw magnesium MT90 (MG-90 acc. to GOST 804-93) is poured in the amount of 1.8 tons from a vacuum ladle and is afterwards heated. On reach 730-740°C of the metal temperature a heated agitator is placed in the crucible, the alloy is left undisturbed in the crucible for 1-1.5 hrs prior to mixing and then mixed for max. 40-50 min; introduced a titanium-containing fusion cake (TU 39-008) being in the compound with barium flux in the proportion of 1:1 is added, mixed again; the temperature of the alloy is then reduced to 710-720°C, the alloy produced was left staying in the crucible for 60 min and thereafter the alloy was sampled for the complete chemical analysis to define Al, Mn, Zn, Si contents and impurities. The alloy composition in wt. %: Al - 2.5-3.4, Mn - min 0.23, Si - 0.8-1.3, Be - 0.0008-0.0012, Zn - min 0.18, Fe - min 0.003.

Industrial applicability

[0026]

Table 1.

Mechanical properties of the magnesium-based alloy at 150°C			
Type of alloy	Creep test		Mechanical properties at 150°C, σ_B MPa
	σ , MPa	Creep ratio σ , %	
AZ91	45.0	0.82	136

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Table 1. (continued)

Mechanical properties of the magnesium-based alloy at 150°C			
Type of alloy	Creep test		Mechanical properties at 150°C, σ_B MPa
	σ , MPa	Creep ratio σ , %	
EN MB MgAl ₂ Si (AS 21)	45.0	0.490	128
EN MB MgAl ₄ Si	45.0	0.540	139
AS 31 alloy claimed	45.0	0.143	128

Table 2.

Level of recovery of alloying elements in magnesium	
Constituents	Recovery level, %
Aluminium	100
Manganese	73.5-96.3; at 720-740°C and time of agitation 40-50 min recovery level of manganese is 80-96%
Silicon	80.8-92.5
Zinc	84.8

Fig. 1 and 2 illustrates the level of recovery of alloying elements in magnesium depending on the temperature and time of agitation.

[0027] Thus, the magnesium-based alloy of said qualitative composition and the method to prepare it facilitate improving mechanical properties of the alloy, particularly, to decrease creep by 3-4 times, reduce production costs due to a better recovery of alloying components in magnesium.

Claims

1. A magnesium-based alloy containing aluminium, zinc, manganese and silicium, wherein the constituents specified are in the following components, wt. %:

Aluminium - 2.5-3.4
Zinc - 0.11-0.25
Manganese - 0.24-0.34
Silicium - 0.8-1.1
Magnesium - rest being

2. A method for producing a magnesium-based alloy that consists in loading alloying components, pouring of molten magnesium, introducing a titanium-containing fusion cake together with a flux agent and continuously agitating said cake, the alloy is soaked and casted, wherein loading the alloying components of aluminium, zinc, manganese and silicium in the form of a ready-made solid master alloy aluminium-zinc-manganese-silicium, after poured in, magnesium is heated, subjected to ageing and stirred afterwards.
3. The method of claim 2, wherein the proportion of the master alloy content to magnesium is 1: (18-20).
4. The method of claim 2, wherein magnesium is heated up to 720-740°C.
5. The method of claim 2, wherein the ageing is carried out within 1-1.5 hrs.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/RU 02/00189

A. CLASSIFICATION OF SUBJECT MATTER C 22 C 23/02, 1/03		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) C 22 C 23/00-23/04, C 22 C 1/02-1/03		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3718460 A (THE DOW CHEMICAL COMPANY), 27.02.1973;	1
Y	I. P. VYATKIN et al. Rafinirovanie I litie pervichnogo maniya, M., Metallurgiya, 1974, pages 54-56, 82-93;	2-5
Y	WO 99/49089 A1 (MAGNESIUM CORP AU PTY et al), 30.09.1999;	2-5
Y	RU 1727403 C (BEREZNIKOVSKY FILIAL VSESOJUZNOGO NAUCHNO- ISSLEDOVATELSKOGO INSTITUTA TI'ANA), 30.11.1994;	2-5
Y	A. V. KURDJUMOV et al. Liteinoe proizvodstvo tsvetnykh I redkikh metallov, M., Metallurgiya, 1982, pages 264-265;	2-5
A	DE 1258106 (MAGNESIUM ELEKTRON LIMITED), 04.01.1968;	1
A	SU 393343 A (O. S. BOCHVAR et al), 27.12.1973;	1
<input type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.		
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Date of the actual completion of the international search (05.09.2002)		Date of mailing of the international search report (19.09.2002)
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